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TRACE ANALYSIS OF ARSENIC BY COLORIMETRY, ATOMIC ABSORPTION AND POLAROGRAPHY

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The precision and accuracy of this polarographic method for determining concentrations of arsenic in water samples were compared to two standard methods, atomic absorption and colorimetry, for observations on replicate analyses of pure standard solutions, split samples from ash ponds, standard reference samples, and standard solutions spiked with potentially interfering elements. The three methods compared favorably for the split samples; however, results of the colorimetric method for the replicate analyses were slightly negatively biased.

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ABSTRACT

A differential pulse polarographic method was developed for determining total arsenic concentrations in water samples from ash ponds at steam-electric generating plants. After digestion of the sample and isolation of arsenic by solvent extraction, the peak current for arsenic is measured and compared to a standard curve. The effective range of concentrations for this method is from 2 to 50 µg/l of arsenic.

The precision and accuracy of this polarographic method for determining concentrations of arsenic in water samples were compared to two standard methods, atomic absorption and colorimetry, for observations on replicate analyses of pure standard solutions, split samples from ash ponds, standard reference samples, and standard solutions spiked with potentially interfering elements. The three methods compared favorably for the split samples; however, results of the colorimetric method for the replicate analyses were slightly negatively biased.

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SECTION 1

INTRODUCTION

Coal ash from steam-electric generating plants contains a small amount of arsenic that probably exists in ash sluice water and settling ponds as the anions arsenite (AsO_3^{-3}) and arsenate (AsO_4^{-3}). Arsenic in these forms can be removed by coprecipitation with ferric hydroxide[1,2] and by precipitation with thionalide;[3] however, some arsenic may be leached into surface or ground waters. The environmental effects of arsenic have been discussed,[4-6] and the National Academy of Sciences recommends that sources of public water supplies contain no more than 0.1 mg/l total arsenic.[5]

Methods for determining concentrations of arsenic in water at trace levels (e.g., 0.1 mg/l) were reviewed in 1975.[6,7] However, since that time, several new methods using atomic absorption spectrometry have been devised.[8-18] This study evaluates those standard reference methods for determining concentrations of arsenic in water that were not discussed or referenced in the reviews in 1975.

For both standard reference methods now used for determining concentrations of arsenic in water,[19-21] the arsenic sample is digested with nitric and sulfuric acid and arsine is generated by adding potassium iodide, stannous chloride, and zinc dust to the digestate. In both methods, arsenic is then isolated by distillation of the gaseous arsine. These methods differ only in the method of determining the concentration of arsenic in the sample. The arsine is measured in one method[20] by colorimetry with silver diethyldithiocarbamate and in the other method[21] by atomic absorption spectrometry with an argon-diluted, air-entrained hydrogen flame.

Because of the similarities in sample preparation which make possible a common bias in these reference methods,[19-21] a third method,[22] which includes a different sample preparation procedure, was selected to confirm the results of analyses by the first two methods. In this third method, the sample is digested in a solution containing a molybdenum(VI) catalyst and nitric, sulfuric, and perchloric acid. After digestion, the resulting arsenate is reduced to arsenite by cuprous chloride in concentrated hydrochloric acid. The resulting arsenic trichloride is then isolated by solvent extraction with benzene.

The arsenic trichloride is back extracted into water, and then the sample is analysed in 1 molar (M) hydrochloric acid by differential pulse polarography.[23] Section 4 of this report describes a method for the analysis of total arsenic by differential pulse polarography with a sample preparation procedure including digestion of the arsenic sample with a molybdenum(VI) catalyst.[23] Although the literature[23] describes a differential pulse polarographic method for determining trace concentrations of arsenic(III) in water, that method does not provide for the analysis of total arsenic that is made possible by digesting the sample with the molybdenum(VI) catalyst.[23]

Although arsenic samples are conventionally digested with nitric and sulfuric acid in the absence of a molybdenum catalyst,[23] such sample preparation procedures must include extreme precautions to prevent the loss of arsenic.[23] This loss of arsenic may be caused by volatilization of arsenic trichloride;[23] however, the volatilization of arsenic in the presence of chloride was not observed by Gorsuch[23] for arsenic samples digested with nitric and sulfuric acid even in the presence of excess organic material.

At sufficiently high concentrations, Ag, Co, Cu, Cr, Hg, Mo, Ni, Pt, and Sb may affect the evolution of arsine.[23,27] Most natural waters, however, do not contain such high concentrations of these elements.[23] These elements may also interfere with measurements by standard colorimetry and atomic absorption,[19-21] but the concentrations at which interference occurs are not known. A recent study[23] evaluated the interference with these measurements when arsine is generated by adding the reductant sodium borohydride rather than potassium iodide, stannous chloride, and zinc dust as in the standard reference methods.[4-6] This study showed that (1) the cations Ag(I), Al(III), Ba(II), Cd(II), Cr(II), Co(II), Cu(II), Fe(III), Pb(II), Mn(II), Mg(II), Ni(II), Sr(II), Sn(II), V(II), and Zn(II), at concentrations of 0.1-11.1 mg/l, do not interfere with the determination of arsenic at a concentration of 1 ug/l; (2) the oxidizing anions CrO_4^{-2}, MnO_4^{-1}, VO_3^{-1}, SiO_3^{-2}, and MoO_4^{-2}, at concentrations between 1.6 and 11.1 mg/l, do interfere, presumably by consuming the reductant sodium borohydride; and (3) the oxidizing anions NO_3^{-1}, PO_4^{-3}, and SiO_3^{-2}, at concentrations less than 11.1 mg/l, do not interfere.

The elements that may interfere with the polarographic determination of arsenic are Cd, Cu, Mo, Pb, Sb(III), Sb(V), Se(IV), Sn(II), Sn(IV), Ti(III), and V(III).[23] Interference from these elements other than copper, which is used to reduce arsenate, is unlikely because of the selectivity in isolating arsenic trichloride by solvent extraction[23] before analysis by differential pulse polarography.[23]

This study evaluates and describes a polarographic method[1,2] and evaluates the standard colorimetric[3,4] and atomic absorption[5,6] methods in (1) determining concentrations of arsenic in effluents from coal-fired steam-electric power plants, (2) assaying standard reference solutions, and (3) assaying for arsenic in the presence of Ag, Cd, Cl, Co, Cu, Cr, Fe, Hg, Mo, Ni, Pb, Sb, Se, Sn, Ti, Ti, and V.

SECTION 2

CONCLUSIONS

A method based on differential pulse polarography was used to determine arsenic at concentrations between 2 and 50 µg/l in water samples collected from ash ponds at coal-fired steam-electric power plants. Samples for arsenic analysis were digested in an acidic solution containing a molybdenum(VI) catalyst, and then the arsenic(V) was reduced to arsenic(III) by cuprous chloride. Arsenic was then isolated by solvent extraction with benzene, back-extracted into water, and quantified in 1 M hydrochloric acid by measuring the differential pulse polarographic current at about -0.4 volts versus a saturated calomel electrode (V vs. sce).

Seven replicate analyses at three concentrations showed that concentrations of arsenic can be determined precisely by either polarography, colorimetry, or atomic absorption. A two-sample t test on the means of the polarographic and colorimetric determinations showed at the 0.05 level of significance that the colorimetric method gives results negatively biased by 1 µg/l at concentrations of 20 µg/l and by 5 µg/l at concentrations of 40 µg/l. Paired-sample t tests showed no significant difference at the 0.05 level among the methods for split samples.

SECTION 3

RECOMMENDATIONS

Colorimetry, atomic absorption, and polarography are recommended methods for determining concentrations of arsenic in ash ponds that receive effluents from steam-electric generating plants. The atomic absorption and colorimetric methods are more efficient, but the polarographic method is better suited for confirmatory analysis.

Further studies should be conducted to determine the applicability of these methods to other process waste streams.

SECTION 4

EXPERIMENTAL

SAMPLE PREPARATION

Field Samples

Field samples were collected in January 1976 from ash ponds at all Tennessee Valley Authority (TVA) coal-fired steam-electric generating plants. These samples were analysed for the presence of arsenic, and samples containing representative concentrations of arsenic were selected for use in this study.

Standard Reference Samples

Standard reference samples for trace metals were obtained from the U.S. Environmental Protection Agency (EPA) and from the U.S. Geological Survey (USGS). EPA standard reference samples, which consisted of concentrated trace metals in very pure acidified water, were diluted to the desired concentrations according to accompanying instructions. Standard reference samples for trace metals were furnished in diluted form by USGS and certified according to the average concentration as determined by several laboratories (interlaboratory certification).

Spiked Samples

Three solutions containing arsenic at a concentration of 50 μg/l were prepared in the laboratory. The first arsenic solution was spiked with Co, Cu, Cr, Fe, Hg, Mo, Ni, Pb, Sb, Se, Sn, Ti, Tl, and V to achieve a concentration of 500 μg/l for each element. The second arsenic solution was spiked with chloride to achieve a chloride concentration of 50,000 μg/l. The third arsenic solution was spiked with silver to achieve a silver concentration of 50 μg/l. All solutions were preserved by spiking with nitric acid to achieve a concentration of 0.2% (v/v, volume expressed as a fraction of total volume). All elements used to spike the arsenic solutions, except mercury, thallium, and chloride were drawn from 1000-mg/l certified atomic-absorption standards (Fisher Scientific Company, Fairlawn, New Jersey). The mercury and chloride concentration used to spike the arsenic solution were prepared according to procedures given in the literature.[19,20] The 1000-mg/l thallium concentration

used to spike the arsenic solution was prepared gravimetrically from thallium chloride powder (1.1735 gram in 1000 ml of reagent water) with weights checked against reference weights certified at the U.S. National Bureau of Standards.

COLORIMETRIC DETERMINATIONS

Arsenic samples for colorimetric determination were digested with nitric and sulfuric acid to yield sulfur trioxide fumes. The digestate was diluted with 25 ml of reagent water, and then the following reagents were added: 5 ml of 12 M hydrochloric acid, 2 ml of 15% (w/w, weight expressed as a fraction of total weight) potassium iodide, and 0.40 ml of 40% (w/v, weight expressed as a fraction of total volume) stannous chloride dihydrate in 12 M hydrochloric acid. After 15 minutes, allowed for reduction of arsenic(V) to arsenic(III), arsine was generated by adding 3 grams of granular zinc (0.5 mm - 12.7 mm pore size). The arsine was reacted with silver diethyldithiocarbamate to yield the red complex for colorimetric measurement.[28] The lead acetate scrubber[28] was not used because sulfide is destroyed by strong oxidising conditions in the digestion. Colorimetric measurements were made with either a Beckman Model B photoelectric spectrophotometer or a Beckman DB-GT grating spectrophotometer.

ATOMIC ABSORPTION DETERMINATIONS

The samples were digested by the same procedure described for colorimetric analysis.[28] After dilution of the digestate with 50 ml of reagent water, the following reagents were added: 8 ml of 12 M hydrochloric acid, 4 ml of 15% (w/w) potassium iodide, and 1 ml of 40% (w/v) stannous chloride dihydrate in 12 M hydrochloric acid. After 15 minutes, allowed for reduction of arsenic(V) to arsenic(III), arsine was generated by injecting 2 ml of a suspension of 13% (w/w) powdered zinc in reagent water. These reagent concentrations[31] were different from those employed by Caldwell et al.[31]

The arsine gas was formed in a 200-ml Berzelius beaker. The zinc slurry was injected through a rubber serum stopper that had been inserted into a glass sleeve fabricated from a test tube and forced through a hole in the rubber stopper for the beaker. The arsine gas was forced from the beaker by sparging with nitrogen through a sintered glass frit into a nitrogen-diluted, air-entrained, hydrogen flame. This apparatus[31] differs from the one described in the literature.[31] Absorbance measurements were made with a Varian Techtron AA-5 atomic absorption spectrometer.

A study was conducted to determine if reaction time would affect the results of analysis of arsenic samples by atomic absorption. After the reagents were added and 15 minutes had

been allowed for reduction of arsenic(V) to arsenic(III), 10 observations were made at 10-minute intervals for a series of 20-ug/l arsenic standards (Table 1). Reappearance of arsenic(V) as a result of reoxidation of arsenic(III) by iodine formed by air oxidation of iodide in the acidic solution was not evidenced by decreasing absorbance measurements.

POLAROGRAPHIC DETERMINATIONS

All measurements were made with the Princeton Applied Research (PAR) Model 174 Polarographic Analyzer with mechanical drop timer and Houston Omnigraphic X-Y Recorder Model 2200-1-1. The dropping mercury electrode was a 2-to-5-second capillary from Sargent-Welch Company with Part No. S-29419. The spectroscopic-grade carbon counter electrode, saturated calomel electrode, outgassing tube, cell holder, cell, and other electrochemical accessories[8] were obtained from PAR.

Nitrogen gas used to deaerate solutions for polarographic analysis was purged of oxygen. Zero-grade nitrogen gas was passed through a furnace containing a special catalytic converter (Model 02-2735 Gas Purifier purchased from Supelco, Bellefonte, Pennsylvania) and heated to 600 degrees Celsius (centigrade, °C). The gaseous effluent from the furnace was successively passed through a Hydro-Purge unit and a Dow gas purifier (available from Applied Science Laboratories, State College, Pennsylvania). The gas was then passed through sintered glass frits in three scrubbing towers; two of the scrubbing towers contained 100 ml of 0.1 M chromous chloride in 2.4 M hydrochloric acid with amalgamated zinc, and the other contained 100 ml of reagent water. The amalgamated zinc was from 0.8-1.2 mm in pore size for a Jones reductor (Fisher Scientific Company, Fairlawn, New Jersey). Details for preparing the chromous chloride scrubbers are given by Meites.[9]

Reagent-grade chemicals were used to prepare all solutions with the exception of the hydrochloric acid that was added to the water extracts for polarographic analysis. This acid was the high-purity "Ultrex" grade from Baker Chemical Company, Phillipsburg, New Jersey. The stock, intermediate, and standard arsenic solutions were prepared from reagent grade arsenic trioxide.[10] The cuprous chloride reagent, 2 N (normal) Cu_2Cl_2 in concentrated hydrochloric acid was prepared by adding 150 ml of concentrated hydrochloric acid, 10 g of copper powder, and 10 g of cuprous chloride powder to a pint bottle containing a Teflon-coated stirring bar. The bottle was immediately stoppered with a Polyseal cap and stirred for 2 hours. After the insolubles had settled, the clear supernatant was siphoned into 15-ml centrifuge tubes containing 0.5 ml of copper powder, and the tubes were immediately sealed with Teflon-lined caps. Just before use, the tubes were centrifuged for 1 minute to produce a

colorless or amber solution. The digestion reagent was prepared by dissolving 2.0 g of sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2H_2O$) in 40 ml of water, adding 50 ml concentrated sulfuric acid, allowing the solution to cool, and then adding 10 ml of 70% perchloric acid.

The samples were digested[22] by adding 1.0 ml of concentrated nitric acid, 2.0-ml of digestion reagent, and four glass beads to 100-ml of the sample in a 500-ml Erlenmeyer flask. The solution was digested at full heat until the solution boiled vigorously, red fumes appeared and dissipated, and white fumes of sulfur trioxide were evolved for 1 or 2 minutes.

CAUTION

Do not evaporate SO_3 fumes longer than specified because the perchloric acid may concentrate to explosive levels. With samples containing excessive organic matter, the amount of nitric acid may be increased or the amount of sample reduced to assure complete digestion and prevent possible explosion.

The method described by Simon et al.[22] was used to reduce arsenate to arsenite with cuprous chloride and to isolate arsenic trichloride by solvent extraction with the following exceptions: the combined benzene extracts were washed by back-extraction with two 3-ml portions and one 4-ml portion of concentrated hydrochloric acid instead of three 4-ml portions, and the arsenic trichloride was isolated by back-extraction into exactly 15.0 ml of reagent water instead of by successive extractions with 9.0 pH buffers.

The isolated arsenic was measured by differential pulse polarography.[23] A 4.0-ml aliquot of the aqueous extract was dispensed into a suitable polarographic cell, and 0.4 ml of high-purity hydrochloric acid was added. After the solution was deaerated for 7 minutes with nitrogen gas treated to remove oxygen, a differential pulse polarographic scan was made between -0.240 and -0.590 V vs. sce under suitable conditions. The peak for arsenic appeared at about -0.4 V. Typical conditions were (1) the mercury head above the capillary (Sargent-Welch Scientific Co., Part No. S-29419) was adjusted to about 45 cm to produce a natural drop time of about 3 seconds in 1 M hydrochloric acid and (2) the PAR Model 174 polarographic analyzer was adjusted as follows: DROP TIME - 2 seconds, SCAN RATE - 2 mV/sec, DISPLAY DIRECTION - positive, SCAN DIRECTION - negative, INITIAL POTENTIAL - (-0.240 V), RANGE - (0.75 V), SENSITIVITY - 1 μA full-scale deflection for 0-2 μg of arsenic and 2 μA for 2-5 μg of arsenic, MODULATION AMPLITUDE - 100 mV, OPERATION MODE - differential pulse, OUTPUT OFFSET - negative

settings between 0 and -450, RECORDER = (Houston omnigraphic X-Y Model 2200-1-3), Y-AXIS = equal to 0.039 V/mm (1 V/in.) and X-AXIS = equal to 1.96 mV/mm (100 mV/in.). To calculate unknown arsenic concentrations in samples, a comparison method was used. The amplitude of electric current was extrapolated from values occurring just before and just after the electrical current peak for arsenic. The extrapolations were compared to a standard curve prepared from analyses of arsenic standards of 0 µg/l, 1.0 µg/l, 2.0 µg/l, 3.0 µg/l, and 4.0 µg/l, and 5.0 µg/l. Standards were analysed by the same methods used to analyse unknown concentrations of arsenic in samples.

SECTION 5

RESULTS AND DISCUSSION

A sensitive differential pulse polarographic method for determining concentrations of total arsenic in water was developed. This method involves digesting a 100-ml sample with nitric, sulfuric, and perchloric acid containing a molybdenum(VI) catalyst; reduction of arsenic(V) to arsenic(III) with cuprous chloride; solvent extraction with benzene to isolate arsenic(III) chloride; back-extraction of the arsenic(III) chloride into water; and measurement of arsenic(III) by differential pulse polarography in 1 M hydrochloric acid. This new method combines the sample preparation for total arsenic described by Simon et al.[4] with the sensitive differential pulse polarographic method described by Meyers and Oysteryoung.[3]

Figure 1 shows typical differential pulse polarograms for standard arsenic concentrations of 0, 10, 20, 30, 40, and 50 µg/l. These concentrations produced peak current readings of 55, 189, 392, 627, 702, and 932 nA, respectively, as determined by extrapolating current values just before and after the peak. A typical least-squares calibration curve prepared from these peak currents is shown in Figure 2, where the least-squares equation is Y = 17.6X + 42.9, Y is the current in nA, and X is the arsenic concentration in µg/l.

The sensitivity of this differential pulse polarographic method for determining concentrations of arsenic is limited by the current produced by the sample blank. If the lowest quantifiable concentration produces a peak current twice that of the least squares sample blank given by the intercept in Figure 2 (85.8 nA), the least-squares equation yields a lowest quantifiable concentration of 2.4 µg/l arsenic. This method using differential pulse polarographic determination is about 20 times more sensitive than coulometric determination with the same sample preparation procedure.[4] This pulse polarographic method for determining concentrations of total arsenic is also about 8 times more sensitive than the 20-µg/l sensitivity reported for differential pulse polarography with raw, undigested samples in 1 M hydrochloric acid and interfering elements present.[3] Meyers and Oysteryoung[3] have achieved sensitivities of 0.2 µg/l with differential pulse polarography in determining concentrations of arsenic in undigested samples with no interfering elements.

The selectivity of the polarographic procedure for total arsenic was demonstrated by quantitatively recovering 20 μg/l (2 μg in a 100 ml sample) of arsenic in the presence of 200 μg/l (20 μg in a 100 ml sample) of selenium(IV), cadmium(II), and lead(II). The latter elements are polarographically active in 1 M hydrochloric acid at voltages sufficiently close to arsenic to interfere.[38]

Copper, which is added in the form of cuprous chloride to reduce the arsenic(V), causes interference if it is not sufficiently removed from the aqueous extract used for polarographic analysis. If present, copper will cause a cathodic charging background that is difficult to offset when scanning for the arsenic(III) peak. Atomic absorption analysis has revealed that most of the extracts for polarographic analysis contained about 0.05 mg/l copper. As much as 0.40 mg/l can be tolerated without affecting recovery of the arsenic, but when the concentration of copper is 0.80 mg/l, only 70% of the arsenic is recovered at 10 μg/l arsenic.

Other digestions were tried unsuccessfully with this polarographic method. Digestion of an arsenic sample with nitric and sulfuric acid[39] was compared to digestion with a molybdenum(VI) catalyst for a standard 50-μg/l arsenic sample. The former method of digestion recovered only 28% of that recovered by digestion with the molybdenum(VI) catalyst. Also, digestion of 100 ml of a standard 50-μg/l arsenic sample with 1 ml of 25% (w/v) potassium persulfate in concentrated sulfuric acid recovered only 14% of that recovered by digestion with a molybdenum(VI) catalyst.

Preliminary test results for arsenic in split samples from ash ponds as analyzed by the colorimetric method[39] and the polarographic method described in Section 4 compare favorably (Table 2). The precision and accuracy of the polarographic,[38,39] colorimetric,[39] and atomic absorption methods[40,41] for determining trace levels of arsenic in seven replicate spiked solutions were determined by comparing test results (Table 3) to a calibration curve prepared by analyzing a series of standard solutions. Table 4 contains the standard deviations, relative standard deviations, means, and percentage accuracies (of the means) for each concentration and method.[38] In addition to these single laboratory tests, the precision of the polarographic method was determined for concentrations of arsenic of 7, 16, 30, and 150 μg/l by a round-robin test with three laboratories with single operators on three days.[38,39] The precision of this method for arsenic in reagent water is given by $S_t = 0.108X + 2.37$ and $S_o = 0.053X + 1.87$, where S_t is overall precision in μg/l, S_o is single operator precision in μg/l, and X is concentration of arsenic in μg/l. The percentage accuracies of the means are -8.6, -0.6, +8.0, and -9.3, respectively.[38] A

version of this polarographic method has been approved by committee ballot as a proposed standard in the American Society for Testing and Materials.[8]

A two-sample t test[17] was performed on some of the data in Table 3 to test the significance of the difference between the means, Δ, assuming that the variances are equal. Figure 3 shows the results of this test for the polarographic and colorimetric methods at 20 µg/l. The t distribution and two-sample t test values shown in Figure 3 were calculated by means of readily available programs.[18] For a Δ of 0, the t value is 3.29. This value is greater than the 2.18 for $t_{0.025}$ for 12 degrees of freedom; therefore, the methods are different at the 0.05 level significance. For a Δ of 1, the t value is 1.37 and the methods agree at the 0.05 level of significance when biased by this amount. Figure 4 shows the t distribution and two-sample t test values for the polarographic and colorimetric methods at 40 µg/l. These data illustrate that the bias of the methods increased to 5 µg/l. The lower results by colorimetry probably were caused by the absence of careful fuming in the digestion.[8] For the polarographic and atomic absorption methods at 10 µg/l, the t value for a Δ of 0 was 0.06, and the methods did not differ significantly at the 0.05 level.

In addition to replicate analyses, the polarographic, colorimetric, and atomic absorption methods for arsenic described in Section 4 were compared for split samples from ash ponds in the Tennessee and Ohio River valleys (Table 5). Background concentration for Ag, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Ti, V, Zn, Cl, and suspended solids (SS) are given in Table 6. The results of analyses reported in Table 6 were performed by standard techniques.[19] The metals were analyzed by digesting the suspended material concentrated onto a 0.45 µm membrane filter and adding this to the value for the dissolved element. The detection limit for the suspended material is lowered by the volume ratio of raw sample to digested material. Because of this, some of the measured values reported for the suspended material are below the detection limit for the dissolved elements.

A paired-sample t test[17] was performed on the split-sample data in Table 5 to determine whether the atomic absorption, colorimetric, and polarographic methods compare favorably at the 0.05 level of significance. For the t test computation, concentrations indicated as less than some value (<) were taken to be zero, and duplicate values were averaged. Figure 5 shows the t distribution for 13 degrees of freedom and t values[18] for the three possible comparisons: (1) polarography vs. atomic absorption, (2) atomic absorption vs. colorimetry, and (3) polarography vs. colorimetry. The calculated t values are much less than 2.16, the t value for 0.025 and 13 degrees of

freedom;[9] therefore, there is no significant difference at the 0.05 level among the three methods.

Comparative tests by colorimetry, atomic absorption, and polarography were made for arsenic in standard reference and synthetic water samples. Test results are given in Table 7. Table 8 includes data for elements other than arsenic in the standard reference samples. Data for arsenic and percentage accuracies[9] by the three methods compare reasonably well with the certified analyses. The same is true for results for the three synthetic samples with potentially interfering elements, [9,25-28]

SECTION 6

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GLOSSARY

A = Ampere.

c= = Centi-, $\times 10^{-2}$ (as a prefix, e.g., cm).

°C = Degrees Celsius (centigrade).

Δ = Difference between the means.

EDTA = Ethylenediaminetetraacetic acid.

g = Grams.

hr = Hour.

in = Inch.

L = Liter.

m = Meter.

µ= = Micro-, $\times 10^{-6}$ (as a prefix, e.g., µl).

m= = Milli-, $\times 10^{-3}$ (as a prefix, e.g., mm).

min = Minute.

M = Molar, mole per liter.

n= = Nano-, $\times 10^{-9}$ (as a prefix, e.g., ng).

N = Normal, equivalent per liter.

% = Percent.

Polarography = Voltammetry at the dropping mercury electrode.

PAR = Princeton Applied Research

sec = Second.

t = Student t statistic.

TVA = Tennessee Valley Authority.

V - Volt.

v/v - Volume expressed as a fraction of total volume.

V vs. scc - Volts versus a calomel electrode filled with saturated potassium chloride.

w/v - Weight expressed as a fraction of total volume.

w/w - Weight expressed as a fraction of total weight.

FIGURES

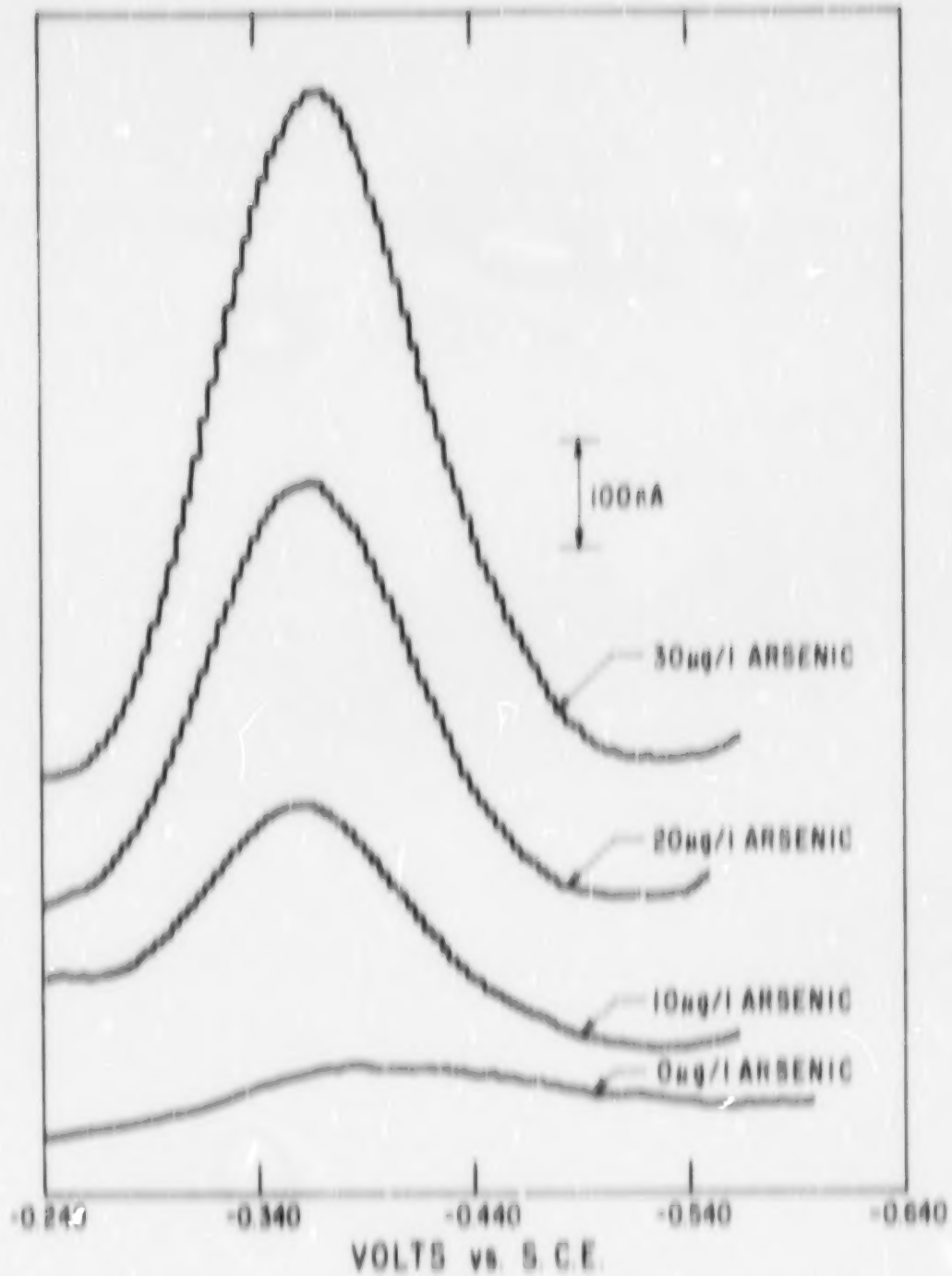

Figure 1. Typical differential pulse polarograms for standard arsenic concentrations

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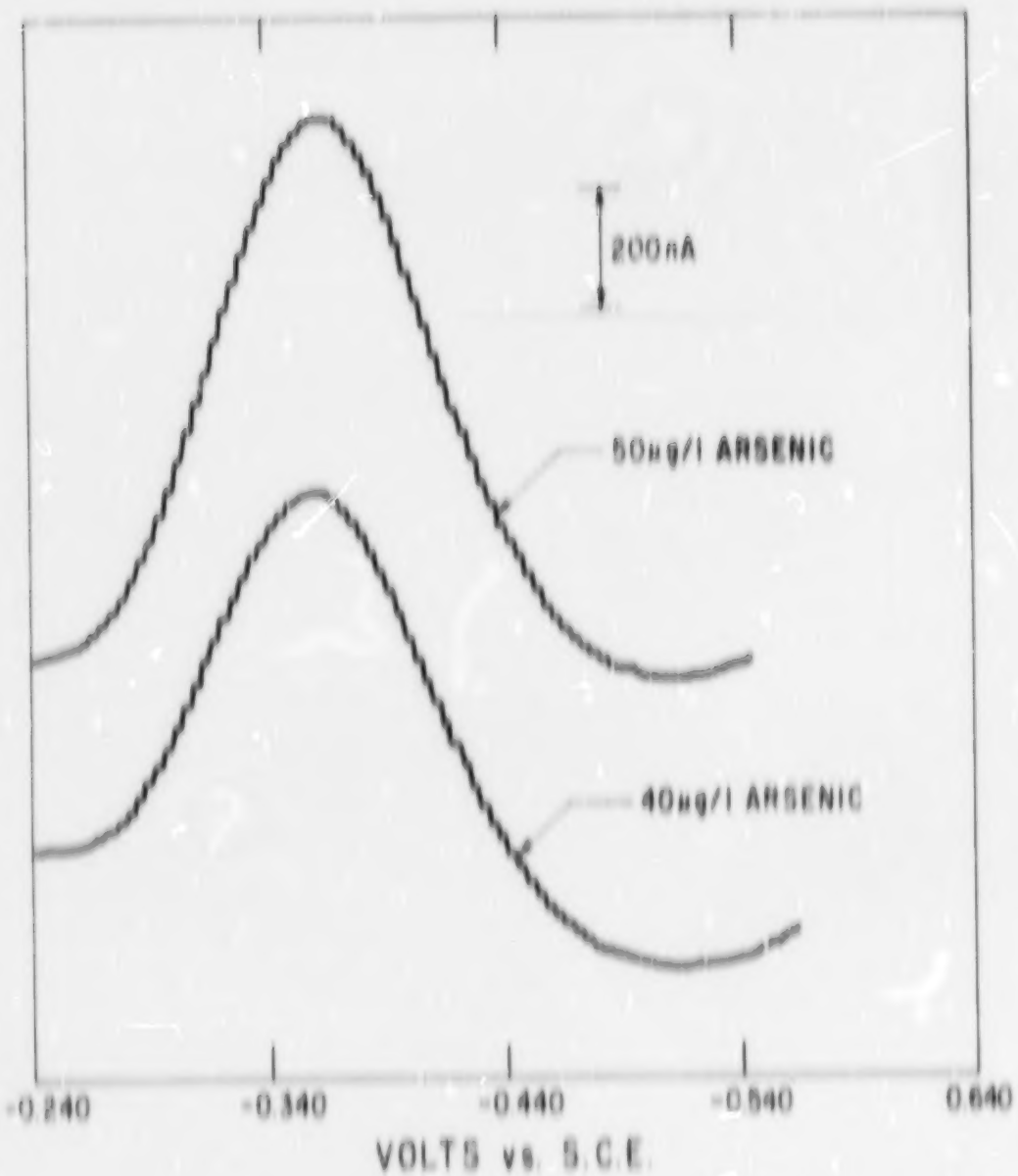

Figure 1. Typical differential pulse polarograms for standard arsenic concentrations (Continued)

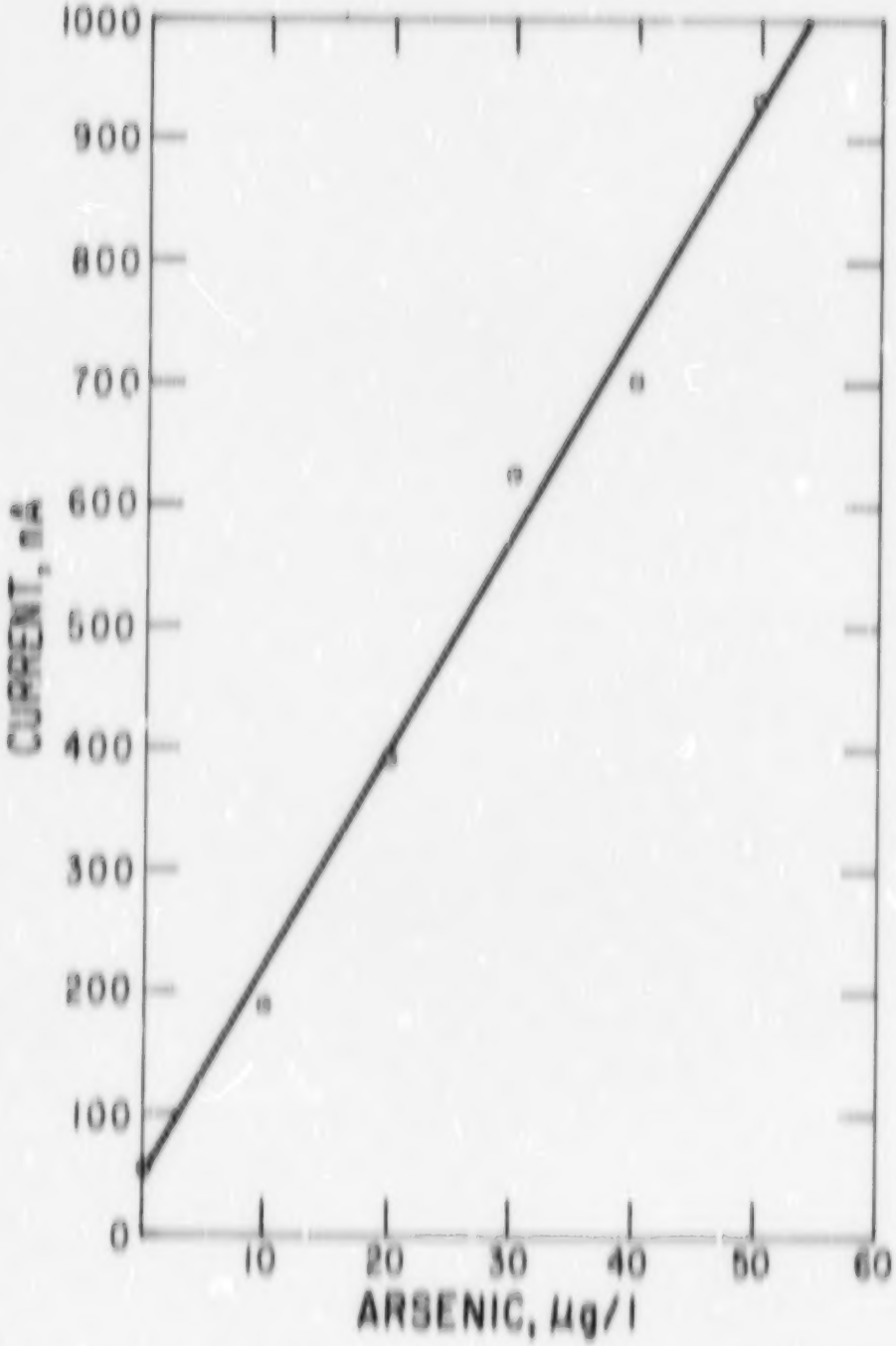

Figure 3. Least-squares calibration curve for total arsenic by differential pulse polarography

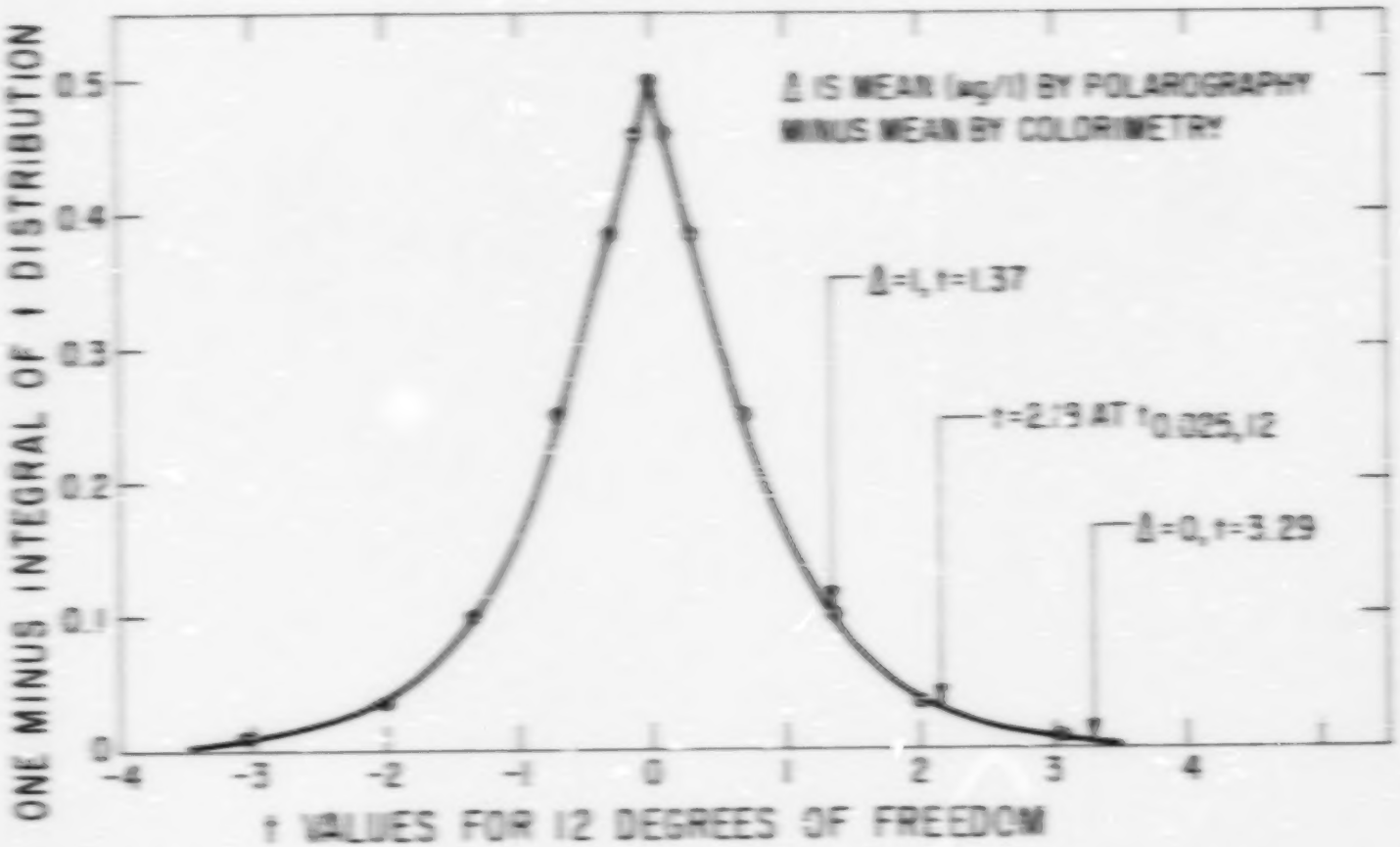

Figure 1. Two-sample t test distribution and values for polarographic and colorimetric determinations for total arsenic in solutions spiked at 20 μg/l

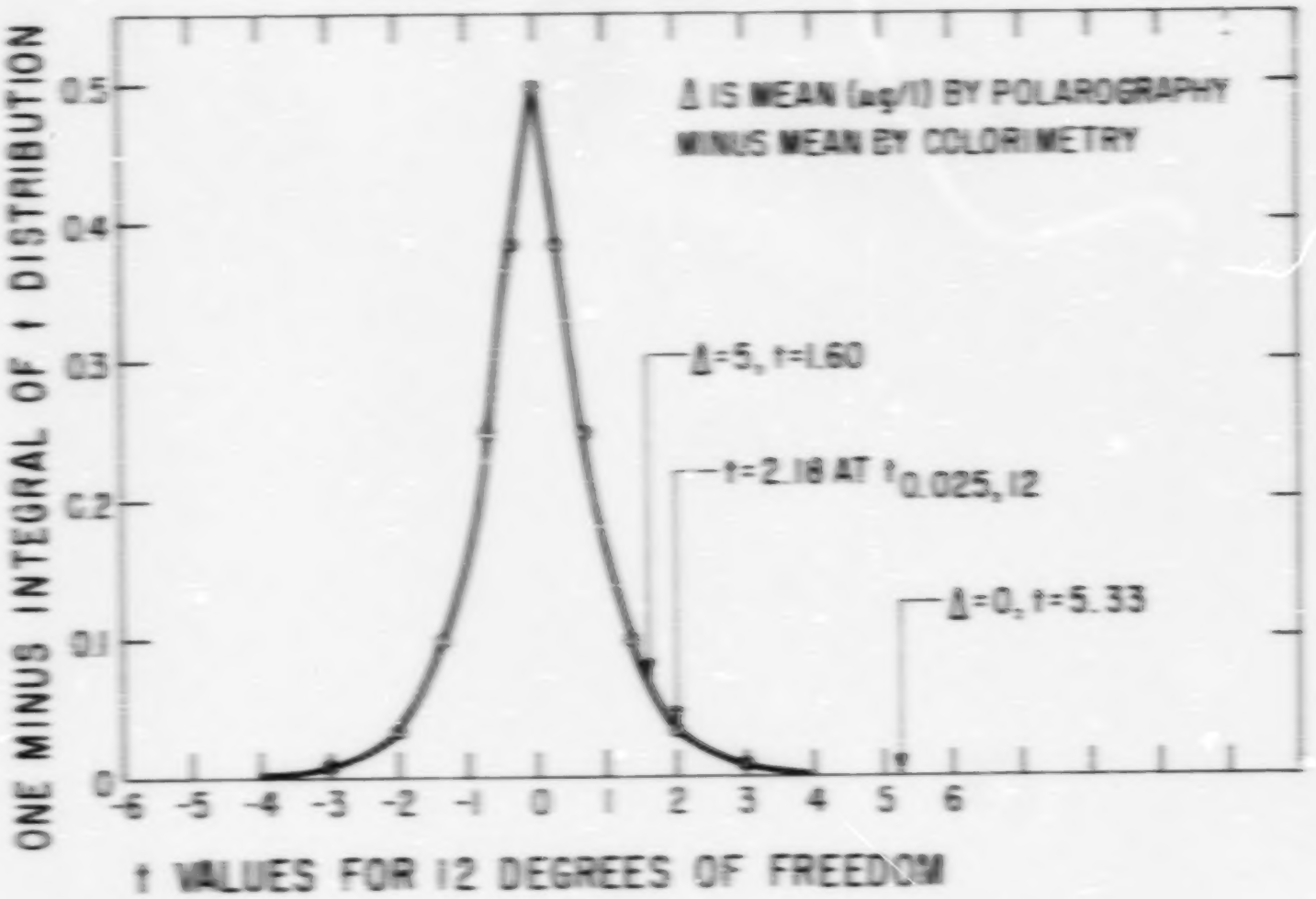

Figure 4. Two-sample t test distribution and values for polarographic and colorimetric determinations for total arsenic in solutions spiked at 40 μg/l

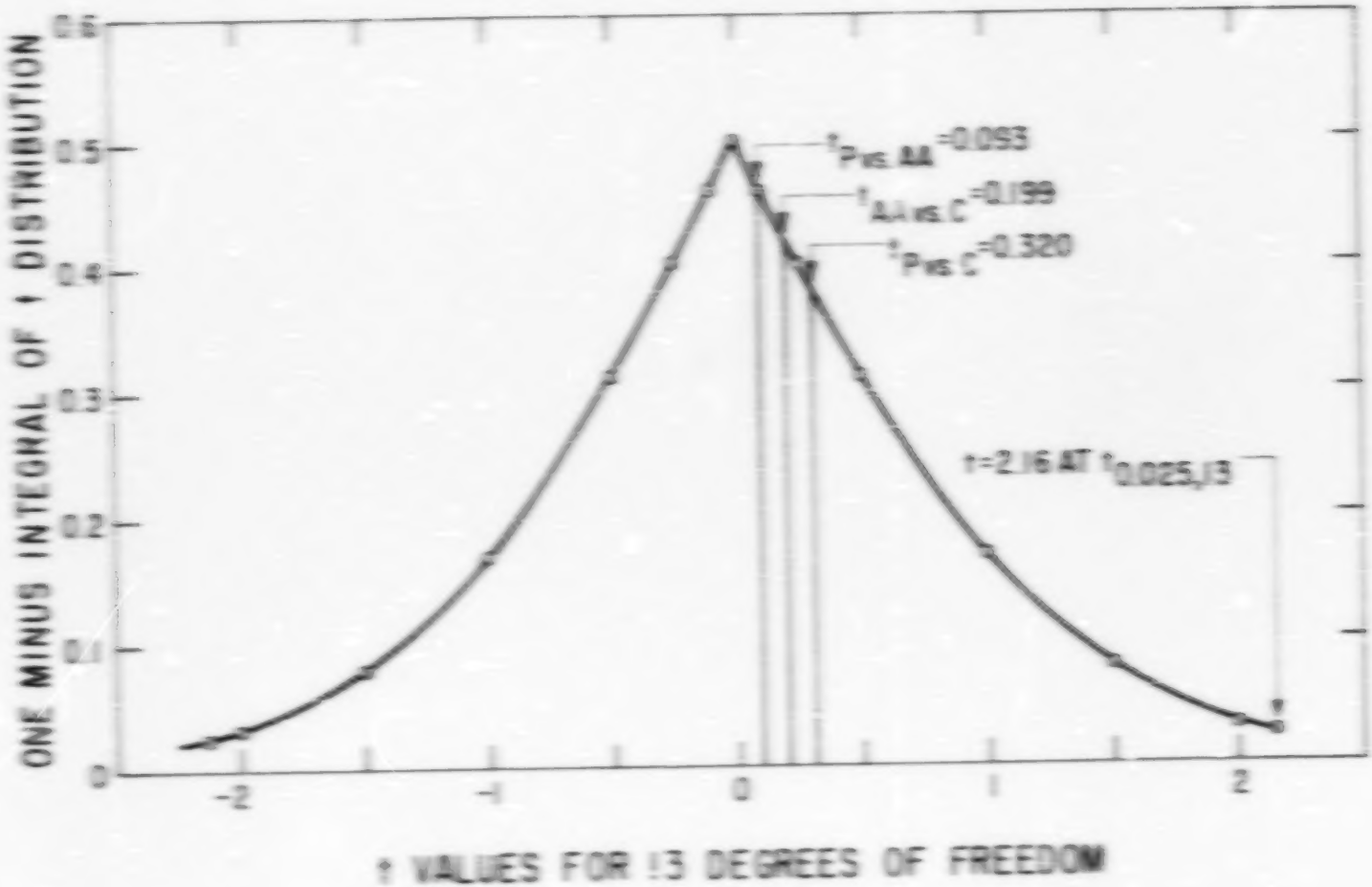

Figure 5. Paired-sample t tests distribution and values for total arsenic in split samples from ash ponds

TABLES

Table 1. EFFECT OF REACTION TIME ON THE ANALYSES OF 20 µg/l ARSENIC SAMPLES BY ATOMIC ABSORPTION

Absorbance	Reaction Time (Minutes)
0.494	10
0.992	20
0.774	30
0.792	40
0.613	50
0.691	60
0.772	70
0.718	80
0.761	90
0.716	100

Time after allowing 15 minutes for reduction of Arsenic(V) to Arsenic(III).

TABLE 2. PRELIMINARY TEST RESULTS OF ARSENIC DETERMINATIONS FOR SPLIT SAMPLES FROM ASH PONDS

Ash Pond	Polarography (µg/l)	Colorimetry (µg/l)
1	123	296
2	38	49
3	99	88
4	88	84
5	68	66

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TABLE 1. ARSENIC DETERMINATIONS FOR REPLICATE SPIKED SURFACE WATER SOLUTIONS

Arsenic Concentration (µg/l)	Arsenic Determination (µg/l)						
Polerography							
0	<2	<2	<2	<2	<2	<2	<2
10	10	7	11	9	8	10	9
20	20	20	18	19	21	20	20
40	39	42	42	41	42	37	41
Colorimetry							
0	<5	<5	<5	<5	<5	<5	<5
10	10	10	10	10	10	10	10
20	18	17	18	18	20	17	18
40	27	36	33	35	34	35	36
Atomic Absorption							
0	<1	<1	<1	<1	<1	<1	<1
2.0	1.5	1.6	1.6	1.6	2.0	1.9	1.0
5.0	6.4	3.7	6.2	6.4	6.3	6.5	6.6
10.0	9.0	9.2	11.0	8.8	9.9	9.9	9.7

TABLE 6. PRECISION AND ACCURACY OF ARSENIC DETERMINATIONS FOR REPLICATE SPIKED SURFACE WATER SOLUTIONS

Arsenic Added (µg/l)	Standard Deviation (µg/l)	Relative Standard Deviation (%)	Mean (µg/l)	Percentage Accuracy (%)
		Polarography		
10	1.4	14.8	9.1	-9.0
20	1.0	4.8	19.7	-1.5
40	1.9	4.8	40.6	+1.5
		Colorimetry		
10	0.0	0.0	10.0	0.0
20	1.0	5.6	18.0	-10.0
40	3.0	8.9	33.4	-16.4
		Atomic Absorption		
2.0	0.3	20.0	1.6	-20.0
5.0	0.8	16.9	4.6	-8.8
10.0	0.7	7.7	9.6	-3.6

TABLE 5. COMPARATIVE TEST RESULTS OF ARSENIC DETERMINATIONS FOR SPLIT SAMPLES FROM ASH PONDS

Location	Polarographic (µg/l)	Colorimetric (µg/l)	Atomic Absorption (µg/l)
Allen	0	10	4.2
Bull Run	40	60	35
Colbert	<5	<1	2
Cumberland	<5	<1	3
Gallatin	50	50	47
John Sevier[a]	237, 280	190	290
John Sevier[b]	157	140	140
Johnsonville	145	160	120
Kingston	143	140	140
Paradise[a]	8	10	9
Paradise[b]	2	5	6.8
Shawnee	179	220	180, 170
Watts Bar	215	130	210
Widows Creek	2	<5	2.6

[a]Samples of water from the fly ash pond were collected at these locations.

[b]Samples of water from the bottom ash pond were collected at these locations.

TABLE 6. CONCENTRATIONS[a] OF ELEMENTS OTHER THAN ARSENIC IN SPLIT SAMPLES FROM ASH BEDS

Location	Ag	Cd	Co	Cr	Cu	Fe	Hg	Mn	Mo	Ni	Pb	Sb	Se	Sn	Sr	V	Zn	Ca	Mg
Allen	<10	12	8	6	31	9400	<0.2	139	180	<50	<5	<100	<2	<1000	<1000	<500	240	12	15
Bell Ranch	<10	<7	3	<5	2	330	<0.2	65	190	<50	<5	<100	10	<1000	<1000	<500	70	4	13
Calhan	<10	<7	2	<5	9	950	<0.2	37	<100	<50	<5	<100	<2	<1000	<1000	<500	<10	6	28
Castlewood	<10	<7	1	<5	<10	20	<0.2	2	460	<50	<5	<100	7	<1000	<1000	<500	<10	5	7
Falcon	<10	<7	3	15	<10	290	<0.2	17	300	<50	11	<100	8	<1000	<1000	<500	<10	6	22
Jules Seeliger Fly Ash	<10	7	9	28	120	970	<0.2	61	220	<50	<5	<100	4	<1000	<1000	<500	32	11	39
Jules Seeliger Bottom Ash	<10	<7	<7	<5	6	1700	<0.2	38	180	<50	<5	<100	3	<1000	<1000	<500	41	11	29
Johnstownville	<10	2	<7	7	4	920	<0.2	6	170	<50	<5	<100	3	<1000	<1000	<500	<10	9	36
Kingston	<10	32	7	<5	59	2650	<0.2	232	<100	<50	<5	<100	<2	<1000	<1000	<500	50	3	23
Pacific Fly Ash	<10	<7	18	170	280	6750	<0.2	440	<100	<50	34	<100	<2	<1000	<1000	<500	790	6	28
Pacific Bottom Ash	<10	<7	3	5	33	9400	<0.2	108	<100	<50	<5	<100	<2	<1000	<1000	<500	67	5	45
Shawnee	<10	3	4	6	<10	1250	<0.2	4	200	<50	<5	<100	2	<1000	<1000	<500	4	8	37
Wacos Bar	<10	3	10	10	42	5700	<0.2	371	<100	<50	<5	<100	<2	<1000	<1000	<500	240	8	20
Widows Creek	<10	<7	1	12	<10	20	<0.2	6	180	<50	<5	<100	2	<1000	<1000	<500	<10	6	4

[a] Concentrations are in ug/L, except Cl and SS (suspended solids) are in mg/L.

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[illegible]

[illegible]

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